

RESOLUTION-ENHANCED FTIR SPECTRA OF RED OAK LIGNIN

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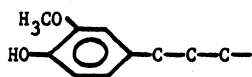
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INTRODUCTION:

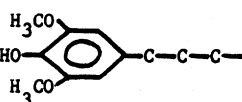
Lignin comprises the complex, amorphous, tridimensional polymeric material obtained from the woody tissues of ferns and all higher plants following chemical degradation of the carbohydrate components. Lignins can be divided into three broad classes:

- 1) softwood or coniferous lignin (from gymnosperms such as pine and fir);
- 2) hardwood lignin (from dicotyledonous angiosperms like oak and beech);
- 3) grass or annual plant lignin (from monocotyledonous angiosperms).

All three classes contain 4-hydroxy-3-methoxyphenylpropane (guaiacylpropane) subunits. The last two classes also have 3,5-dimethoxy-4-hydroxyphenylpropane (syringialpropane) subunits. Annual plants exhibit, in addition, a third building-block: 4-hydroxyphenylpropane.



Guaiacyl-



Syringial-

Lignin imparts structural rigidity in woody tissues of plants and in cell walls. In the manufacture of paper from wood pulp, lignin is often treated simply as a waste by-product. In the soil, lignin from decaying plant matter is assumed to be an important source of humic substances and thus of critical importance in soil fertility.

E. J. Jones published the first comprehensive infrared spectroscopic investigation of lignin in 1948 [1]. In the decades since, numerous other infrared studies [2] have supplemented the information gathered by more traditional chemical and physical methods. The structural complexity of these biopolymers, as well as the multiplicity of intra- and intermolecular hydrogen bonds have somewhat limited the usefulness of infrared spectroscopy for determining structure and composition. Fourier transform infrared (FTIR) technology now offers the high signal-to-noise and frequency accuracy prerequisite to uncovering significant data buried under the broad, overlapping bands typically observed in the spectra of such complex biomaterials. Two resolution-enhancement techniques have proved invaluable in this regard: namely, (a) Fourier deconvolution and (b) second-derivative spectroscopy. The importance of these methods has recently been strikingly demonstrated for such varied materials as coals [3], proteins [4], and humic acids [5]. This paper reports the use of these procedures to elicit new details from the spectrum of an organosolv lignin.

EXPERIMENTAL:

Preparation of the Red Oak lignin sample: Forty grams of red oak wood chips (oven-dried) were cooked in 240 mL of 50% (w/w) ethanol/H₂O with 0.214 g H₂SO₄. Next the samples were heated to 195 °C for a short period of time and then cooled immediately. The final cooking liquor was diluted with two volumes of H₂O to precipitate the lignin. After filtration, the precipitate obtained was redissolved in 50% ethanol/H₂O and twice reprecipitated by H₂O dilution. This step insured the elimination of soluble contaminants, principally hemicellulose sugars.

FTIR spectra: The infrared spectrum (4000-400 cm⁻¹) of a KBr pellet of the lignin was collected, as previously described [5]. The spectrum consisted of 1000 scans at

2 cm⁻¹ instrument resolution. Second derivative and Fourier-deconvolved spectra were calculated in the same manner as reported for a humic acid [5].

RESULTS AND DISCUSSION:

The Figure presents the FTIR spectrum of red oak lignin from 1900-700 cm⁻¹. The bottom curve represents the original spectrum, the middle curve the deconvolved data, and the top curve the second derivative of the original spectrum. Clearly, both resolution-enhancement techniques substantially increase the observable spectral detail. (In this region alone, there are 16 new peaks.) In addition, measured peak frequencies from both procedures closely agree with one another. Table I summarizes observed band frequencies and their suggested assignments.

As noted in Table I, bands between 1800 and 1620 cm⁻¹ result from carbonyl and olefinic stretching vibrations. The 1713 cm⁻¹ band is indicative of unconjugated ketones (Absence of a band near 2755 cm⁻¹ rules out the presence of aldehydes.) The low intensity relative to that of the 1515 cm⁻¹ aromatic ring stretch suggests that no more than 1/4 to 1/3 of the subunits have such carbonyl groups. A new, very weak feature at 1685 cm⁻¹ may indicate a few conjugated carbonyls. The 1657 cm⁻¹ band is typical of the C=C stretch for *trans*-disubstituted olefins; the 1641 cm⁻¹ peak, along with features at 3079, 3036, 993 and 914 cm⁻¹, signifies the presence of vinyl groups. Most of these very weak bands are not visible in the original spectrum of the organosolv lignin.

Aromatic ring-stretching vibrations and methoxy and methylene deformations occur between 1610 and 1320 cm⁻¹. Typical lignin IR spectra only exhibit one band near 1610 cm⁻¹. In contrast, the resolution-enhanced data clearly shows two peaks, one at 1611 and the other at 1591 cm⁻¹. The first is characteristic of syringial groups; the latter of guaiacyl moieties. Other assignments are given in the Table.

In the CH stretching region between 3100 and 2800 cm⁻¹ (not shown) there are several important features. The deformation overtone at 2840 cm⁻¹ results from methoxy groups, as do the CH₃ stretches at 2964 and 2879 cm⁻¹. Bands at 2937 and 2916 cm⁻¹ are characteristic of symmetric CH₂ stretching modes. At 3079 cm⁻¹ is a very weak band probably due to vinyl groups. Another at 3036 cm⁻¹ is also typical of olefins. Weak features at 3060 and 3005 cm⁻¹ are due to aromatic CH stretches; bands at 2985 and 2896 cm⁻¹ result from alkyl CH stretching modes.

CONCLUSIONS:

Resolution-enhancement techniques now permit a more complete interpretation of the IR spectrum of a lignin than ever before. Of particular interest is the new evidence of vinyl and *trans*-disubstituted olefinic groups in this organosolv lignin. The techniques described should prove invaluable in future studies of lignins not only from plant materials but also from soils.

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TABLE I: Observed mid-IR bands of hardwood lignin (cm⁻¹)

Beech*	Red Oak Lignin		Tentative Assignment [2,6,7]
	ORIG	XRSLN	
1720	1713	1765	C=O str, unconjugated ketone
.	.	1715	
.	.	1700sh	
.	.	1685	C=O str, conjugated ketone
.	.	1672	C=O str, {conjugated acid ?; conjugated aldehyde ?
.	.	1657	C=C str, <u>trans</u> -disubstd olefin
.	.	1641	C=C str, vinyl; <u>cis</u> -disubstd olefin
1609	1609	1611	Ar ring str: S
.	1594sh	1591	Ar ring str: G
1510	1513	1515	Ar ring str: G, S
.	.	1497sh	Ar ring str:
1460	1462	1464	CH ₂ def
.	1454sh	1454	Ar ring str: G, S
.	.	1446sh	OCH ₃ sym def
1425	1425	1424	CH ₂ def, {vinyl; Ar ring str ?; adjacent to carbonyl
.	.	1393	CH ₂ def, <u>cis</u> -disubstd olefin ?
1365	1374sh	1374	CH ₃ sym def, substd olefin ?
.	.	1366	Ar ring str ?
1325	1326	1331	Ar ring str: S
.	.	1308sh	
1270	1270	1269	C-O str, Ar-OR: G
.	1248sh	1243	: S
1220	1215	1216	C-O str, Ar-OR: S
.	.	1193	
.	.	1184	
.	1150	1152	: G
1120	1115	1117	: S
1090sh	1086sh	1091	C-O str, ArO-R: S
.	.	1064sh	
1030	1031	1032	C-O str, ArO-R: G
.	.	993	CH ₂ twist, vinyl
970	.	964	CH ₂ def, <u>trans</u> -disubstd olefin
.	913	914	CH ₂ wag, vinyl
870	.	.	
.	847	845	Ar CH out-of-plane def: G
.	825	822	Ar CH out-of-plane def: S

*Data from ref. 8. Abbreviations: ORIG = original spectrum; XRSLN = resolution enhanced (2nd derivative/deconvolution); S = syringial; G = guaiacyl; Ar = aromatic; sym = symmetric; str = stretch; def = deformation; disubstd = disubstituted; sh = shoulder.

